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INFLUENCE OF THE PREPARATION METHOD ON THE MICROSTRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF THE $(Ca,Bi)_3Co_4O_{9+\delta}$ COBALTITES

The ceramic samples of the $(Ca,Bi)_3Co_4O_{9+\delta}$ were prepared using solid-state reactions and citrate methods. The influence of the preparation method on the crystal and microstructural, physicochemical and functional characteristics of these materials was studied. The temperature-time processing regimes of the $(Ca,Bi)_3Co_4O_{9+\delta}$ ceramics were selected. It is found that $Ca_{2.8}Bi_{0.2}Co_4O_{9+\delta}$ solid solution, which was prepared by a citrate method, demonstrated the maximal value of the power factor (240 $\mu W/(m \cdot K^2)$ at 1,100 K) among the ceramics prepared. It is shown that citrate method has significant advantages in comparison with the solid-state reactions one because it allows to reduce energy consumption during the synthesis and at the same time to prepare more dense, fine-grained, and electrically conducting ceramics with a lower linear thermal expansion coefficient and higher power factor.

Introduction. Layered calcium cobaltite $Ca_3Co_4O_{9+\delta}$ is the prospective material for the high-temperature thermoelectroconversion because it possesses high thermoelectric characteristics, relative low cost and is stable in air at high temperatures [1].

Functional characteristics of the ceramics based on $Ca_3Co_4O_{9+\delta}$ can be improved by means of the partial substitution of calcium cations by bismuth cations in its structure [2, 3] as well as by using of "soft" preparation methods [3–5], which are alternative to the solid-state reactions method; so, development of the chemical modification methods of the layered calcium cobaltite by means of "soft", low-temperature methods of synthesis is very important for the state-of-art thermoelectric materials chemistry.

In this work influence of the preparation method on the crystal structure, microstructure, thermal expansion, electrical conductivity and thermo-EMF of ceramic samples of $(Ca,Bi)_3Co_4O_{9+\delta}$ cobaltites.

Experimental technique. The $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ (x = 0.0; 0.2) ceramics was prepared by means of solid-state reactions method (*A* samples) and citrate method (*B* samples).

A samples were prepared from $CaCO_3$ (pure grade), Bi_2O_3 (pure grade) and Co_3O_4 (pure grade), which were mixed in the $(9 - 3x) : 3x : 4$ molar relations in the Pulverizette 6 planetary mill ("Fritsch", Germany) with ethanol addition, pressed at 0.13 MPa pressure into pellets having 25 mm diameter and 3–5 mm thickness and annealed during 12 h at 1,173 K. After annealing pellets were grinded in Pulverizette 6 mill (with ethanol addition), re-pressed at 0.26 MPa pressure into bars having 5×5×30 mm dimensions and sintered during 4–20 h at 1,193 K.

To synthesize the *B* samples we used the $Ca(NO_3)_2 \cdot 4H_2O$ (pure for analysis) (C = 0.6 M), $Bi(NO_3)_3$ (was prepared by dissolution of Bi_2O_3 (pure grade) in HNO_3 (conc.)) (C = 0.6 M), $Co(NO_3)_2 \cdot 6H_2O$ (pure for analysis) (C = 0.8 M) and $C_6H_8O_7$ (pure grade) (C = 0.5 M) water solutions, which were mixed in the $(1 - x) : x : 1 : 5$ volume relations. Obtained solutions were evaporated at 343 K to prepare viscous pink gel (during solution evaporation the intensive NO_2 evolution was detected, which took place due to the HNO_3 decomposition).

Pink gel was dried at 383–403 K on the electroheating plate by caramel-like mass formation. This mass was grinded and dried in an oven during 2 h at 423 K and again grinded. Obtained grey-magenta powder was annealed during 4 h at 873 K. Formed at this stage black powder was thoroughly grinded and pressed into pellets and bars, which were annealed during 4–10 h within 1,123–1,173 K temperature region with following sintering during 4–20 h at 1,183 K.

Identification of the samples and determination of their lattice constants using X-ray diffraction analysis (XRD) (diffractometer D8 Advance Bruker AXS (Germany), CuK_α-radiation) and IR absorption spectroscopy (Furier-spectrometer Nexus ThermoNicolet) were performed. Optical density of solutions (*B* samples) was fixed by means of CFK-3-01 fotometer.

Thermal analysis of the $CaCO_3$ and Co_3O_4 powders mixture as well as the powder of precursors at synthesis of $Ca_3Co_4O_{9+\delta}$ by citrate method after drying at 403 K was conducted by means of the Mettler Toledo (Swiss) thermal analysis system in air within 298–1,173 K temperature region at 10 $K \cdot min^{-1}$ heating rate.

Granulometric composition of the mixture of $CaCO_3$ and Co_3O_4 powders and powder of precursor at synthesis of $Ca_3Co_4O_{9+\delta}$ by citrate method after its annealing at 873 K was determined by means of Analysette 22 MicroTec Fritsch GmBH (Germany) particle laser analyzator. Microstructure of the sintered ceramics was studied using JSM-5610 LV (Japan). Apparent density of the samples (ρ_{exp}) was determined using their mass and geometric dimensions.

Thermal expansion, electrical conductivity (σ) and thermo-EMF(*S*) of ceramics was measured in air within 300–1,100 K temperature region using methods described in [6, 7]. Power factor values of ceramics were calculated using equation of $P = S^2\sigma$. Linear thermal expansion coefficient (LTEC, α) and apparent activation energy of electrical conductivity (E_a) values of the samples were calculated from the linear parts of $\Delta l / l_0 = f(T)$ and $\ln(\sigma T) = f(1 / T)$ dependences respectively.

Results and their discussion. As can be seen from the Fig. 1, absorption spectra of solutions used at synthesis of ceramics by citrate method during their evaporation did not changed practically. So, we can conclude, that chemical transformations do not take place at "solution stage" of citrate method and this stage results only in homogenization of the samples on the molecular level (nanolevel).

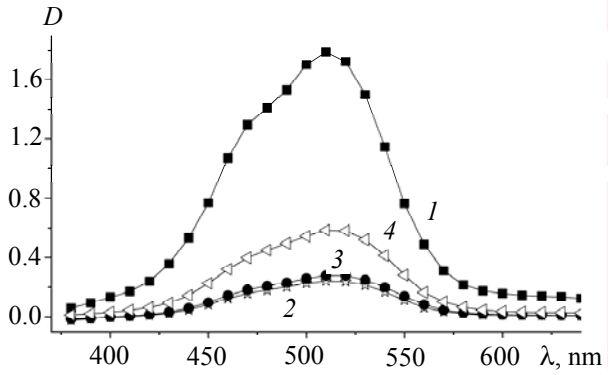

Fig. 1. Absorption spectra of the initial solution $Co(NO_3)_2 \cdot 6H_2O$ (*1*), mixture of $Ca(NO_3)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $C_6H_8O_7$ (*2*) solutions and this mixture after its evaporation during 2 h (*3*) and 8 h (*4*)

The size of particles of mixture of $CaCO_3$ and Co_3O_4 powders after milling in the planetary mill varied within 0.4–15 μm and fractions with particle sizes of 0.7–0.9 μm, 2–3 μm and 7–8 μm (Fig. 2, *a*) were maximal. Particle size of $Ca_3Co_4O_{9+\delta}$ (sample *B*) precursors powder after annealing at 873 K and grinding in an agate mortar varied within 0.2–15 μm and fractions with particle sizes of 0.6–0.7 μm, 1–2 μm and 8–9 μm (Fig. 2, *b*) were maximal. Taking into account that large-sized fraction (8–9 μm) of the *B* sample contains not the $CaCO_3$ and Co_3O_4 individual particles, but their aggregates (agglomerates), on the base of granulometric analysis results we can conclude that size of individual particles in the *A* powder is large than in the *B* one.

The results of the thermal analysis of the reaction mixtures are given in the Fig. 3. As can be seen, thermogravimetric curve (TG) of the mixture of $CaCO_3$ and Co_3O_4 powders (Fig. 3, *a*) may be divided in four stages and on the 1st–3rd stages mass of the sample decreased but on the 4th stage mass increased.

The mass loss of the sample on the 1st and 2nd stages is small (≈0.37 and ≈0.21% within $298 < T < 473$ K and $473 < T < 893$ K temperature regions respectively) and take place, probably, due to the evolution from the sample adsorbed and weakly-bonded water as well as, perhaps, decomposition of $CaCO_3$ particles forming the small-sized fraction ($0.7 < d < 0.9$ μm). The intensive (≈20.06% or ≈10.12 mg, which is close to the calculated mass loss – ≈10.72 mg) mass loss begins at 893 K. It follows by the large endothermic effect with extremum at 1,083 K (Fig. 3, *a*, DSC curve) and corresponds to the $CaCO_3$ decomposition (according to [8], calcium carbonate decomposition in air begins near 900 K). On this stage forms the product of reaction – layered calcium cobaltite:

$$3CaCO_3 + {}^4/_3Co_3O_4 + (1 - {}^3/_2\gamma) / 3O_2 \rightarrow$$

$$\rightarrow Ca_3Co_4O_{9-\gamma} + 3CO_2\uparrow.$$

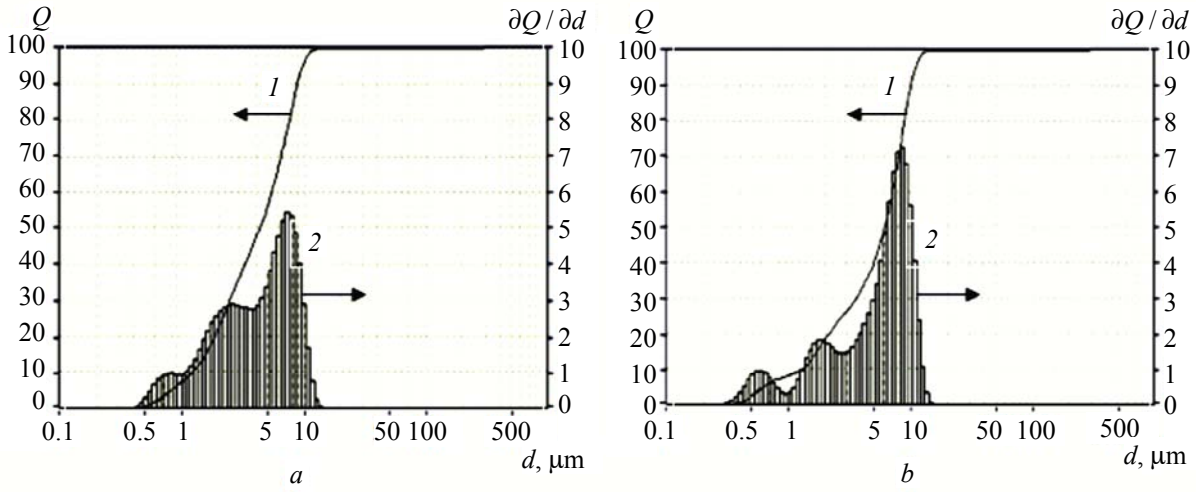

Fig. 2. Integral (*1*) and differential (*2*) distribution curves of the particles of the calcium carbonate $CaCO_3$ and cobalt oxide Co_3O_4 mixtures (*a*) and $Ca_3Co_4O_{9+\delta}$ precursor prepared by citrate method (*b*)

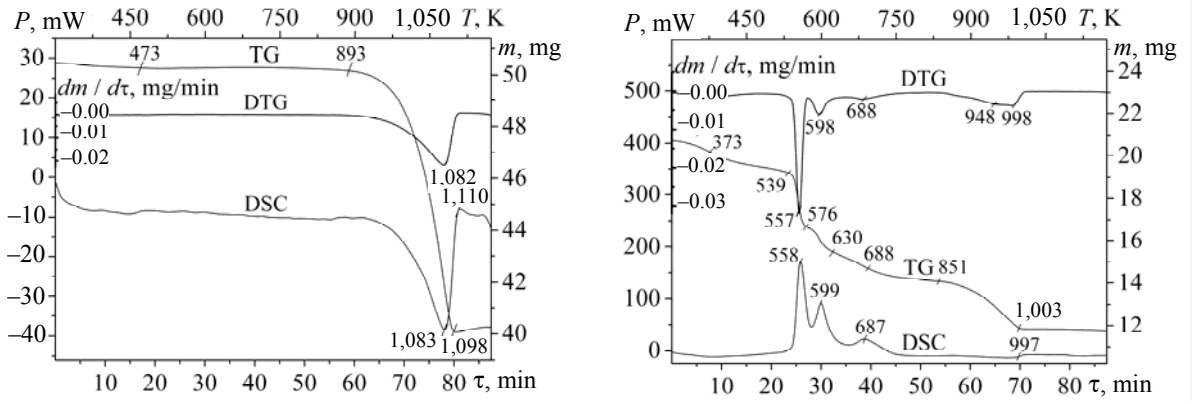

Fig. 3. Results of the thermal analysis of the calcium carbonate $CaCO_3$ and cobalt oxide Co_3O_4 mixture (*a*) and $Ca_3Co_4O_{9+\delta}$ precursor prepared by citrate method (*b*)

Mass gain at the fourth stage of the TG curve (1,098 < *T* < 1,197 K) (≈0.41%), which follows bythe small diffuse exothermic effect with extremum at 1,110 K, took place due to the saturation of the calcium cobaltite with oxygen:

$$Ca_3Co_4O_{9-\gamma} + (\gamma + \delta) / 2O_2 \rightarrow Ca_3Co_4O_{9+\delta}.$$

Decomposition of the $Ca_3Co_4O_{9+\delta}$ precursor obtained by the citrate method (sample *B*) has more complex character; TG curve consisted of the eight parts (Fig. 3, *b*). On the first two stages of the process the mass loss is ≈2.72% (298 < *T* < 373 K) and ≈4.83% (373 < *T* < 539 K), which corresponds to the evolution from the sample the free and bonded water respectively [4].

Mass loss of the powder on the thirth –sixth stages (≈11.95% at 539 < *T* < 576 K, ≈6.03% at 576 < *T* < 630 K, ≈2.92% at 630 < *T* < 688 K and ≈3.79% at 688 < *T* < 851 K), following by the large exothermic effects with extrema at 588, 599 and 687 K, took place due to the step-by-step oxidation of the calcium ($Ca_3[C_3H_4(OH)(COO)_3]_2$) and cobalt ($Co_3[C_3H_4(OH)(COO)_3]_2$) citrates into $CaCO_3$ and Co_3O_4 [4, 5] according to the equations

$$Ca_3[C_3H_4(OH)(COO)_3]_2 + 9O_2 \rightarrow$$
$$\rightarrow 3CaCO_3 + 9CO_2\uparrow + 5H_2O\uparrow,$$
$$Co_3[C_3H_4(OH)(COO)_3]_2 + 9{,}5O_2\uparrow \rightarrow$$
$$\rightarrow Co_3O_4 + 12CO_2\uparrow + 5H_2O\uparrow$$

by the atmospheric oxygen as well as by the oxygen, which evolved at the calcium and cobalt nitrates decomposition:

$$Ca(NO_3)_2 \rightarrow CaO + 2NO_2\uparrow + {}^1/_2O_2\uparrow,$$
$$3Co(NO_3)_2 \rightarrow Co_3O_4 + 6NO_2\uparrow + O_2\uparrow.$$

Mass loss on the seventh stage (≈10.70% at 851 < *T* < 1,003 K) follows by the diffuse endothermic effect with extremum at 997 K and corresponds to the calcium carbonate decomposition with formation of the reaction product – $Ca_3Co_4O_{9+\delta}$ [4, 5]:

$$3CaCO_3 + {}^4/_3Co_3O_4 + ({}^1/_3 + \delta / 2)O_2 \rightarrow$$
$$\rightarrow Ca_3Co_4O_{9+\delta} + 3CO_2\uparrow.$$

On the eighth stage the mass loss is small (≈0.39% at 1,003 < *T* < 1,197 K) and corresponds, probably, to the finishing of reaction of the $Ca_3Co_4O_{9+\delta}$ formation.

After finishing of the synthesis *A* sample was mono-phase, within X-ray accuracy, and had structure of $Ca_3Co_4O_{9+\delta}$ (Fig. 4, curve *5*). Obtained by us its lattice constants (Table 1) are in a good accordance with the literature data: a = 0.48376(7) nm, b_1 = 0.45565(6) nm, b_2 = 0.28189(4) nm, c = 1.0833(1) nm, β = 98.06(1)° [9].

As can be seen from Fig. 4, formation of the $Ca_3Co_4O_{9+\delta}$ in the *B* sample begins at 873 K (curve *2*) and practically finishes after sample annealing during 4 h at 1,123 K (curve *3*).

So, using of the citrate method allows us to essentially decrease of temperature (for 50 K) and time of the synthesis (up to 3 times) of calcium cobaltite.

Table 1

Values of the lattice constants of the $(Ca,Bi)_3Co_4O_{9+\delta}$ cobaltites

Composition	a, nm	b_1, nm	b_2, nm	c, nm	β, grad	V, nm^3	b_1 / b_2
$Ca_3Co_4O_{9+\delta}$ (*A*)	0.4836(5)	0.4561(5)	0.2821(5)	1.083(1)	98.19(5)	0.2365(7)	1.617
$Ca_3Co_4O_{9+\delta}$ (*B*)	0.4830(7)	0.4562(8)	0.2812(6)	1.085(1)	98.28(8)	0.2365(10)	1.622
$Ca_{2.8}Bi_{0.2}Co_4O_{9+\delta}$ (*A*)	0.4849(7)	0.4579(7)	0.2833(6)	1.087(1)	98.30(7)	0.2389(9)	1.617
$Ca_{2.8}Bi_{0.2}Co_4O_{9+\delta}$ (*B*)	0.4856(6)	0.4596(7)	0.2854(9)	1.086(1)	98.21(6)	0.2398(8)	1.610

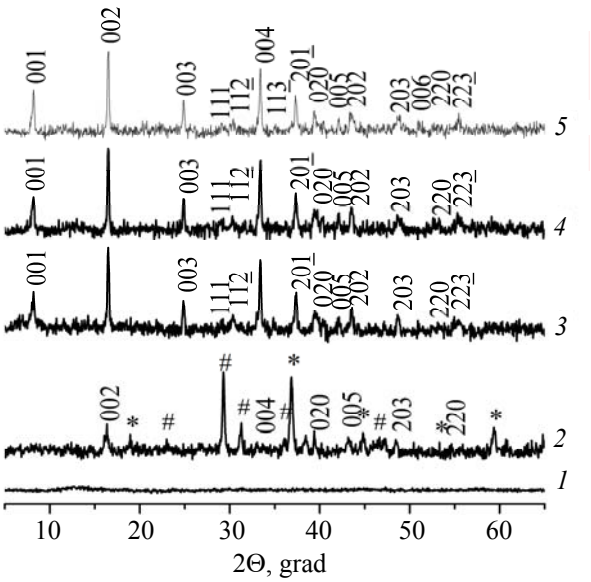

Fig. 4. X-ray diffractograms of the $Ca_3Co_4O_{9+\delta}$ powders: *1* – dried at 423 K sample *B*; *2* – annealed at 873 K during 4 h sample *B*; *3* – annealed at 1,123 K during 4 h sample *B*; *4* – annealed at 1,123 K during 10 h and at 1,183 K during 8 h sample *B*; *5* – annealed at 1,173 K during 12 h and at 1,193 K during 12 h sample *A*; * – $CaCO_3$; # – Co_3O_4

From the presented in Table 1 data is followed, that lattice constants of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ (x = 0.0; 0.2) cobaltites do not depend practically on the preparation method and increase at partial substitution of calcium by bismuth (according to [10], for C.N. = 6 $R(Bi^{3+}) > R(Ca^{2+})$).

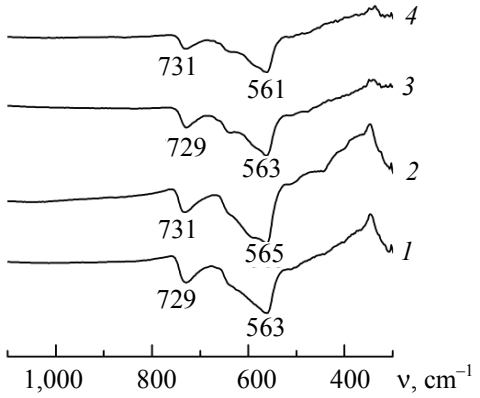

Fig. 5. IR absorption spectra of the $Ca_3Co_4O_{9+\delta}$ (*1*, *2*) and $Ca_{2.8}Bi_{0.2}Co_4O_{9+\delta}$ (*3*, *4*) powders obtained by solid-state reactions (*1*, *3*) and citrate methods (*2*, *4*)

On the IR absorption spectra of the $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ powders two absorption bands with extrema at 561–565 cm^{-1} (ν_1) and 729–731 cm^{-1} (ν_2) were observed, which corresponded to the stretching vibrations of Co–O (ν_1) and Ca(Bi)–O (ν_2) bonds in their structure [4]. IR absorption spectroscopy results are in a good accordance with X-ray data and show that prepared by means of solid-state reactions and citrate methods $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ samples are identical.

To use in praxis, $Ca_3Co_4O_{9+\delta}$ and its derivatives should be prepared in the form of high-dense ceramics. Sinterability of ceramics improves at increasing of temperature (T_{sint}) and time of the sintering. Sintering temperature of $Ca_3Co_4O_{9+\delta}$ is limited by the temperature of its peritectic melting (1,199 K [11]). Effect of the sintering time on the density of ceramics is given in Fig. 6, which shows that maximal density of the *A* ceramics is ≈2.7 g/cm^3 and is reached after sintering during 12 h at 1,193 K, whereas density of the *B* samples reaches value of ≈3.2 g/cm^3 after sintering during 8 h at 1,183 K.

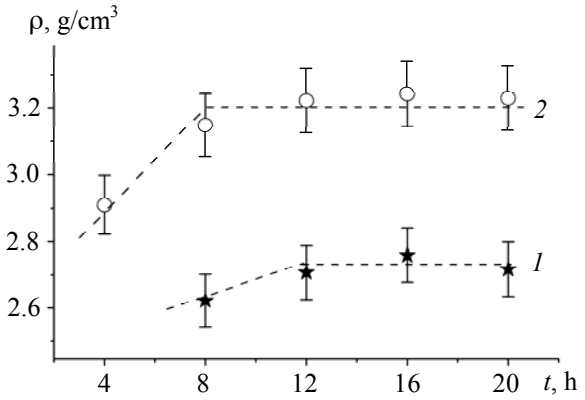

Fig. 6. Dependence of the apparent density (ρ) of $Ca_3Co_4O_{9+\delta}$ ceramics versus time of sintering (t): *1* – sample *A*, T_{sint} = 1,193 K; *2* – sample *B*, T_{sint} = 1,183 K

The $Ca_3Co_4O_{9+\delta}$ crystallites were plate-like and had average dimensions of 3.1×2.4×0.9 μm and 2.5×1.7×0.5 μm for samples *A* and *B* respectively. The large sides of crystallites were oriented, preferentially, perpendicular to pressure direction (Fig. 7).

Comparing the results of X-ray analysis, densitometry and electron microscopy, we can conclude, that using of citrate method let us obtain more dense and fine-grained ceramics with reduced energy consumption in comparison with solid-state reactions method.

The $\Delta l / l_0 = f(T)$ dependences for the samples studied were linear practically; so, within 300–1,100 K temperature interval the $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ oxides demonstrated any structural phase transitions. As can be seen from the data given in Table 2, LTEC values of the samples reduced at partial substitution of calcium by bismuth and for ceramics prepared by means of citrate method were less than for samples synthesized by means of solid-state reactions method due to the lower porosity values of the formers.

a

b

Fig. 7. Microfotographs of the surface of the $Ca_3Co_4O_{9+\delta}$ ceramics (perpendicular to the pressure direction): *a* – sample *B*; *b* – sample *A*

The results of the study of electrophysical and thermoelectric properties of the $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ layered cobaltites are given in Fig. 8. As can be seen, all the oxides studied are the *p*-type semiconductors ($\partial\sigma / \partial T > 0$, $S > 0$, Fig. 8, *a*, *b*), hereby the conductivity character of un-substituted $Ca_3Co_4O_{9+\delta}$ phase above 900 K changes to the metallic ($\partial\sigma / \partial T < 0$) due to evolution of the weakly-bonded oxygen (δ) from the volume of ceramics to the environment. Conductivity values for ceramics prepared using citrate method were larger than for samples synthesized by means of the solid-state reactions method (Fig. 8, *a*) due to the less porosity of the former. The values of apparent activation energy of electrical conductivity of the samples studied increased at substitution of calcium by bismuth and for $Ca_{2.8}Bi_{0.2}Co_4O_{9+\delta}$ solid solution prepared by means of citrate method were larger than for ceramics synthesized by means of solid-state reactions method (Table 2).

Table 2

Values of LTEC (α), apparent activation energy of electrical conductivity (E_a) and apparent density (ρ) of the $(Ca,Bi)_3Co_4O_{9+\delta}$ ceramics

Composition	$\alpha \cdot 10^5$, K^{-1}	E_a, eV	ρ, g/cm^3
$Ca_3Co_4O_{9+\delta}$ (*A*)	1.29	0.069	2.73
$Ca_3Co_4O_{9+\delta}$ (*B*)	1.28	0.065	3.20
$Ca_{2.8}Bi_{0.2}Co_4O_{9+\delta}$ (*A*)	1.17	0.089	2.36
$Ca_{2.8}Bi_{0.2}Co_4O_{9+\delta}$ (*B*)	1.15	0.105	2.50

Thermo-EMF values of $Ca_{3-x}Bi_xCo_4O_{9+\delta}$ ceramics increased at substitution of calcium by bismuth (at high temperatures) and did not depend practically on the preparation method of ceramics (Fig. 8, *b*).

The power factor values of thermoelectric oxides investigated increased at temperature increasing, at partial substitution of calcium by bismuth and for the samples prepared using citrate method were essentially larger than for ceramics synthesized using solid-state reactions method (Fig. 8, *c*). The maximal value of power factor demonstrates the $Ca_{2.8}Bi_{0.2}Co_4O_{9+\delta}$ ceramics obtained using citrate method – 240 $\mu W/(m \cdot K^2)$ at 1,100 K.

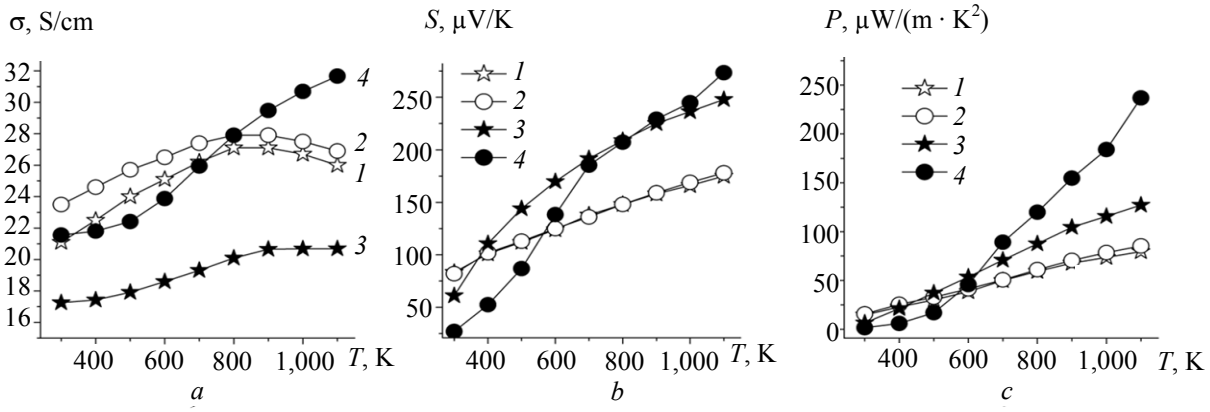

Fig. 8. Temperature dependences of electrical conductivity (σ) (*a*), thermo-EMF (*S*) (*b*) and power factor (*P*) (*c*) of the $Ca_3Co_4O_{9+\delta}$ (*1*, *2*) and $Ca_{2.8}Bi_{0.2}Co_4O_{9+\delta}$ (*3*, *4*) ceramics obtained by solid-state reactions (*1*, *3*) and citrate methods (*2*, *4*)

Conclusion. The influence of the preparation method and partial substitution of calcium by bismuth on the crystal structure, microstructure, physico-chemical and thermoelectric properties of ceramic samples of $(Ca,Bi)_3Co_4O_{9+\delta}$ phases was investigated. It was found that maximal value of the power factor among the ceramics synthesized (240 μW/(m · K^2) at 1,100 K) had $Ca_{2.8}Bi_{0.2}Co_4O_{9+\delta}$ solid solution prepared using citrate method. It was shown that using of citrate method let us reduce the energy consumption at synthesis and obtain more dense, fine-grained and electrically conducting ceramics with a lower linear thermal expansion coefficient and larger power factor.

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